



Effects of particle dispersion on photocatalysis probed by the effect of platinum on dichloroacetic acid oxidation by P25 and nanoparticulate rutile

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ARTICLE INFO

Article history:

Available online 19 May 2010

Keywords:

Photocatalysis
Titanium dioxide
Rutile
P25
Platinum
Dichloroacetic
Antenna
Dispersion

ABSTRACT

Oxidation of dichloroacetic acid (DCA) by two titanium dioxide catalysts (P25 and a nanoparticulate rutile (NR)) was measured at pH 3 and the results compared with parallel measurements on the same TiO₂s modified by deposition of platinum.

Although the platinum loading corresponded to less than one platinum crystallite for each TiO₂ crystal, platinization significantly increased photocatalytic activity – 30-fold in the case of NR, high area rutile. This has been attributed, by ourselves [7] and others, e.g. [9], to the increased efficiency of hole-generation as a consequence of electron trapping by the platinum.

Each catalyst was then milled, and UV–vis transmission spectra were used to show that milling improved the catalyst dispersion. Milling unplatined TiO₂ caused either insignificant decreases (P25) or increased activity (NR). This contrasts with the previously reported [16] significant decrease in activity for propan-2-ol oxidation. The difference is attributed to a different dependence on UV intensity of DCA degradation and propan-2-ol oxidation. DCA oxidation rate increased linearly with UV intensity, *I*, whereas propan-2-ol oxidation varies as *I*^{0.5}.

However, milling did decrease significantly the rate of DCA oxidation by both of the platinized catalysts, especially by the platinized rutile. It is suggested that most of the UV is absorbed by TiO₂ crystals that have no platinum, but that in poorly dispersed TiO₂, UV-generated electrons may be transported along a chain of TiO₂ crystals to a platinized TiO₂ at which they are trapped. This is analogous to the antenna model postulated by Bahnemann and co-workers [15]. It is proposed that milling breaks down the antennae. Consequently electron transport is disrupted and the effectiveness of electron trapping by platinum is reduced and the measured photoactivity decreases.

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1. Introduction

Studies of the liquid phase photo-oxidation of organic molecules by TiO₂ have shown that the photocatalytic activity is generally limited by rapid recombination of photogenerated charge carriers [1–4]. Deposition of noble metals (Pt, Ag, Au) on the surface of titania and other wide-band semiconductors often, but not always, increases photoactivity [5–8]. The metal is considered to provide an electron sink [8] which by reducing recombination facilitates degradation of organics by both direct hole transfer (e.g. to dichloroacetic acid) [7,9,10] and by hydroxyl radical intermediates (e.g. propan-2-ol oxidation) [1,5,8]. Platinum usually gives

the biggest benefit, probably because it provides the most effective electron sink, as has been demonstrated for ZnO nanodots [11]. The degree of photocatalytic enhancement also depends on the structural properties of the molecule to be oxidized and, for Ag/TiO₂, Amal and co-workers proposed that higher enhancements occur with lower ratios of C–H:C–O/C=O bonds [12]. When noble metal deposition reduced catalytic activity, the metal loadings were often high and the reduction has been attributed to both blocking of active surface sites [13] and to optical effects [14]. The present paper builds on an earlier study of dichloroacetic acid (DCA) oxidation [7] which demonstrated that although platinum deposition on Degussa P25 increased photoactivity by a significant extent (70%) the increase resulting from deposition on rutile was much larger (3700%). In both cases the maximum enhancement was at levels of platinum which corresponded to much less than one platinum crystallite per TiO₂ crystal. An enhancement of catalytic activity at platinum levels below one metal crystallite per titania had been reported previously by Bahnemann and co-workers [15] who suggested that this implied an ‘antenna effect’ through which electrons trapped by the metal crystallite on one titania crystal of a flocculate

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influence the oxidation by holes at the surface of separate titania crystals indirectly linked to the first by a loose flocculate structure.

Although the degree of flocculation/agglomeration in titania dispersions inevitably modifies the measured photoactivity, this aspect of photocatalysis receives little attention. The measured activity of a very poorly dispersed titania is expected to be low because the available surface is poorly utilized. In better dispersed systems more subtle effects can be expected because the slurry optics depend on the catalyst particle size. Egerton and Tooley showed that the improvements in the TiO_2 dispersion, brought about by milling either nanoparticulate rutile or Degussa P25 suspensions, increased the UV absorption and reduced the rate of propan-2-ol oxidation [16]. They argued that stronger UV absorption caused more photons to be absorbed by each of a proportionately smaller number of crystals. At the intensities used by them, the photocatalytic oxidation of propan-2-ol varies as the square root of the number of photons absorbed within a crystal, as expected if charge-carrier recombination limits photoactivity [1,16]. Consequently, increased UV absorption within a TiO_2 crystal caused increased recombination and this reduced the measured oxidation rate.

The present study extends earlier work [7,9] on the effect of platinization on the photocatalytic oxidation of DCA by investigating the influence of the TiO_2 dispersion. The dispersion of either P25 or nanoparticulate rutile was varied by lightly milling both untreated and platinized catalysts in a way that had been demonstrated not to form the surface defects that have been shown to be introduced by prolonged heavy milling [17]. Changes induced by milling in the UV-vis transmission of the suspensions were monitored using a spectrometer fitted with an integrating sphere. DCA degradation was chosen as a test reaction because oxidation of DCA, unlike that of propan-2-ol [1,16] varies with UV intensity, I , as I^1 [7,9]. It was judged that this would allow the contribution of charge carrier transportation along antennae [15] to be more clearly separated from the effects of recombination caused by changes in the UV absorption by individual crystals [16]. It was also hoped that the low ratios of C–H:C–O/C=O bonds in DCA would lead to significant rate enhancement as a consequence of platinization.

2. Experimental methods

2.1. Materials

Nanoparticulate rutile (NR) supplied by Uniqema (now Croda Chemicals) was prepared by TiCl_4 hydrolysis and is similar to the high area rutile described elsewhere [7,16]. The nitrogen BET area

was $\sim 120 \text{ m}^2 \text{ g}^{-1}$. Powder X-ray diffraction showed no phases other than rutile. P25 (Degussa, $\sim 80\%$ anatase, 20% rutile, $50 \text{ m}^2 \text{ g}^{-1}$ [18]) was used as received. The platinum precursor was K_2PtCl_6 (Fluka, $40 \text{ wt}\%$ Pt). Dichloroacetic acid (Alfa Aesar, 99%), sodium nitrate and sodium hydroxide (both Riedel de Haen, puriss) were used as received from the suppliers.

2.2. Preparation of Pt/ TiO_2 catalysts

The preparation of the Pt/ TiO_2 by photodeposition from platinum in solution has been described previously [7]. The platinum content, $0.38 \text{ wt}\%$ Pt(II) or $0.38 \text{ wt}\%$ Pt(0), of the nanoparticulate rutile catalysts was that previously found to give optimum enhancement of DCA oxidation [7]. The platinum content of $0.15 \text{ wt}\%$ Pt(II) on P25 was selected to give approximately the same surface concentration of platinum taking into account the lower area of P25. This compensation is not exact because the platinum particles on P25 are slightly larger than those on the high area rutile (see below) and consequently their surface area is smaller. However, further refinement was deemed unnecessary because the differences in enhancement of DCA degradation caused by 0.15% and 0.38% Pt(II) on P25 are small, $\sim 10\%$ [7].

TEM images of the platinized catalysts are shown in Fig. 1. Examination of many fields of view suggests that on rutile the platinum particles are $6\text{--}10 \text{ nm}$ diameter and on P25 are slightly larger ca. $12\text{--}14 \text{ nm}$. Although these are larger than the $2\text{--}4 \text{ nm}$ crystallites reported by other authors reasons for the differences have not been sought.

2.3. Milling procedure

Unmilled TiO_2 /DCA dispersions were prepared by mixing the TiO_2 with the DCA solution in the reaction vessel. Milled dispersions were produced by adding 1 g of catalyst and 40 cm^3 of 36 mM DCA to the small scale mill-pot used previously [16]. 50 g of glass ballotini ($180\text{--}212 \mu\text{m}$) was then added and the mixture was agitated by an impellor at 900 rpm for a defined time during which the ballotini collided with TiO_2 aggregates and broke them down either into smaller aggregates or into primary crystals. The milled TiO_2 /DCA suspension was decanted from the ballotini which were subsequently washed with 36 mM DCA to retrieve residual catalyst. The washings were added to the suspension which was then made up to 250 cm^3 with 36 mM DCA.

The size distribution of a separate preparation of nanoparticulate rutile was measured using an X-ray disc centrifuge (Brookhaven Instruments, B1-XDC) in which a centrifugal force,

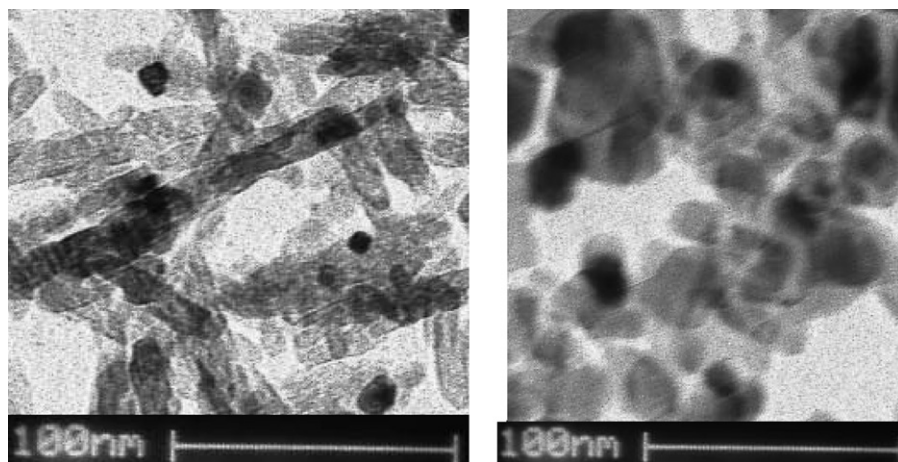


Fig. 1. TEM images of Pt/rutile (left) and Pt/P25 (right).

induced by spinning the disk, sediments the particles at a rate which is monitored by measuring the attenuation of a collimated X-ray beam. The particle size distribution is then calculated from Stokes Law. Although the derived figures may significantly underestimate the true size, because of uncertainty in the density of flocculated particles, it was clear that milling decreases particle size, as detailed previously [16]. Measurements were made on aqueous dispersions milled with a silicate dispersant. In a typical experiment the mean size of an untreated nanoparticulate rutile had a nominal mean size of 29 nm after milling of 30 min. No measurements have been made on samples of the nanoparticulate rutile surface treated with platinum, but when a nanoparticulate rutile surface treated with silica was milled for 30 min the measured size decreased from 1000 nm to 70 nm. Even though both the 29 nm for untreated rutile and the 70 nm for surface treated rutile are probably underestimates, they are both larger than the ~10 nm estimated from the surface area, or the 7 nm from X-ray line broadening.

2.4. Measurement of dichloroacetic acid (DCA) oxidation

The degradation of DCA at pH 3 was followed by measuring the concentration of chloride ions in the reaction mixture with an ion selective electrode as described previously [7]. 1 g of catalyst was dispersed in 250 ml of 36 mM DCA and 2 ml of 5 M sodium nitrate (NaNO_3) was added to adjust the ionic strength so that the electrode response was not affected by minor changes in total electrolyte concentration. Preliminary measurements showed that above 2 g dm^{-3} TiO_2 the activity was insensitive to the catalyst loading. Prior to irradiation, the pH of the suspension was adjusted to pH 3 with 1 M NaOH and the suspensions were mixed (using a magnetic stirring bar) for 30 min with a constant flow of oxygen into the reactor. After 30 min a UV lamp (Philips PL-L 36W 09 actinic lamp) with a peak intensity at 360 nm was placed in an axially located well within the reactor. This well was surrounded by water-jacket. For those experiments in which the dependence of DCA oxidation on light intensity was investigated (see Fig. 4), the intensity incident on the DCA solution was controlled by filling the jacket with an appropriate concentration of 2-nitrophenol solution (Fig. 1). The amount of UV light transmitted was quantified by UV–vis spectroscopy of the 2-nitrophenol solutions used. A pH of 3 was chosen in order to optimize adsorption of the DCA (which exists mainly as the dichloroacetate anion at this pH) on the surface of the TiO_2 (which is positively charged at this pH) and because it has been shown that, at pH 3 the rate of degradation of the DCA anion varies linearly with the UV intensity [9]. Replicate experiments showed a repeatability within $\pm 5\%$.

2.5. Measurements of 250–750 nm spectra

Spectra of TiO_2 suspensions in a 2 mm path length cell were measured using a Cary 5000i spectrophotometer equipped with a DRA-2500 integrating sphere to collect scattered light. Reflectance measurements were made using a BaSO_4 disk as a standard and transmission measurements were made relative to a black disk.

3. Results

3.1. The effect of milling on the optical transmission of suspensions of nanoparticulate rutile and P25

The milling conditions were selected to improve the dispersion of the TiO_2 slurries and hence change their optical characteristics. The spectra of the resulting milled suspensions were measured using an integrating sphere to collect both scattered and unscattered (directly transmitted) light. The results for suspensions of nanoparticulate rutile (NR) (Fig. 2a) demonstrated that milling in

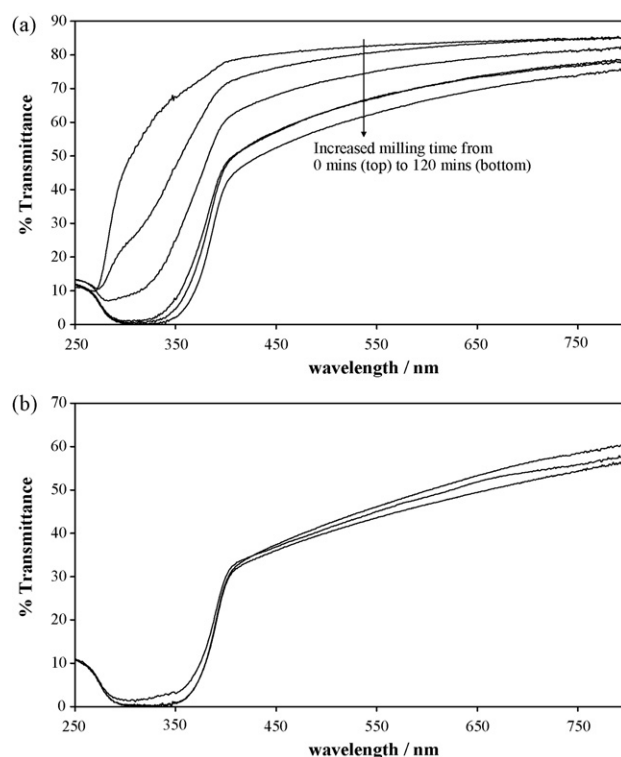


Fig. 2. (a) Transmittance profiles for dispersions of nanoparticulate rutile milled for increasing time. From the top, the milling times are 0, 5, 15, 30, 60 and 120 min. (b) Transmittance profiles for P25 dispersions milled for increasing time. From the top the milling times are 60, 15 and 0 min.

DCA solution decreases the transmittance (increases the absorption) of the suspension. The transmissions of the unmilled P25 suspensions (Fig. 2b) were lower than that of unmilled NR and for P25 the increases in absorption caused by milling were very small. This implies that initially the unmilled rutile was more aggregated than the P25 and that the NR agglomerates were too big to scatter visible light effectively but that the dispersion of NR was significantly improved by milling, whereas the dispersion of P25 altered very little. This conclusion broadly parallels that for dispersions of these two titanias in propan-2-ol [16].

3.2. The effect of milling on DCA oxidation by P25 and nanoparticulate rutile

Preliminary experiments showed that no degradation occurred in the absence of irradiation and also demonstrated that, in the absence of TiO_2 , irradiation of pH 3 DCA solutions did not generate chloride ions. By contrast, as shown in Fig. 3a and b, irradiation of suspensions in DCA of both nanoparticulate rutile and of P25 led to a steady increase in the chloride ion concentration which did not deviate significantly from linearity even when ~40% of the DCA was oxidized. As shown in Fig. 4, the rate of degradation on nanoparticulate rutile increased linearly with light intensity, which was monitored by measuring the 365 nm transmission of the nitrophenol solutions surrounding the lamp. This confirms the similar conclusions obtained by. Hufschmidt et al. [9] in a study of P25.

The results for the nanoparticulate rutile (Fig. 3a and Table 1) show a clear increase in the measured photoactivity when the catalyst is milled. Milling for 60 min increases the activity by a factor of ~3.5. The corresponding results for P25 are shown in Fig. 3b which demonstrates that before milling the activity for P25 is ~15 times that of NR. However, milling the P25 suspensions caused negligible change in the reaction rate of lightly (15 min) milled sus-

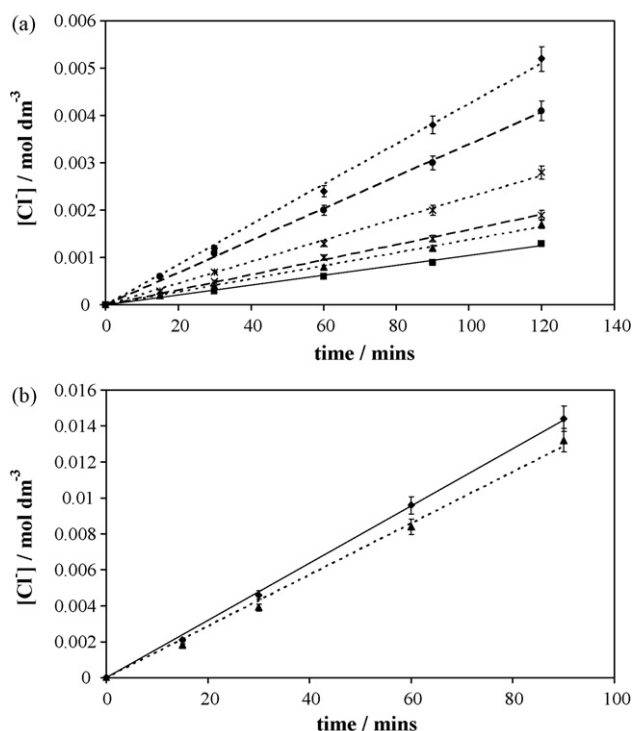


Fig. 3. (a) Photogeneration of Cl^- ions from DCA at pH 3 during UV irradiation of 4 g dm^{-3} suspensions of nanoparticulate rutile (NR). The suspensions were milled for 120 min, ♦; 60 min, ●; 30 min, ✕; 15 min, x; 5 min, ▲. Results for the unmilled suspension designated by the ■ symbol. (b) Photogeneration of Cl^- ions during irradiation of 4 g dm^{-3} suspensions of P25 in solutions of DCA at pH 3 and the difference in reaction rate of P25 suspensions that had been milled for 0 min (♦) and 60 min (▲), prior to irradiation. (As the 0 and 15 min lines superimpose the 15 min line has been omitted.).

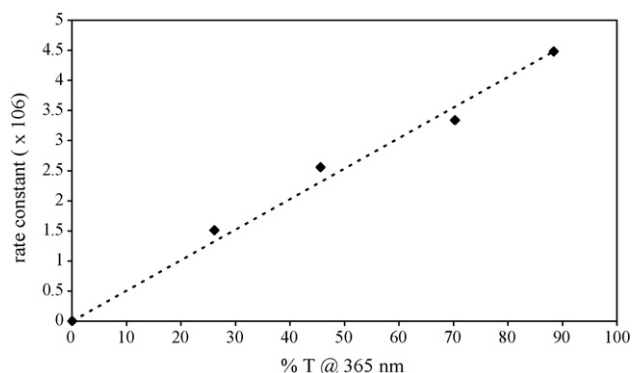


Fig. 4. The dependence of the rate of degradation of DCA oxidation by nanoparticulate rutile on UV intensity. The dashed line shows the best fit linear correlation ($R^2 = 0.99$).

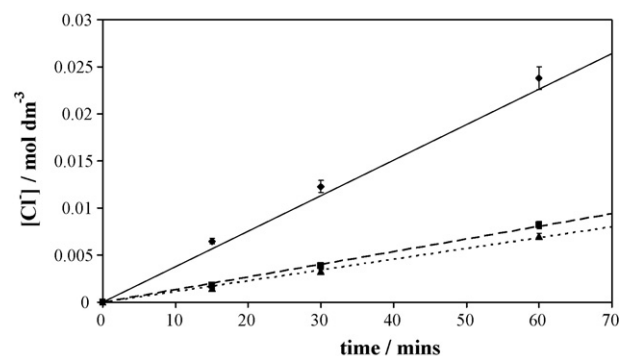


Fig. 5. DCA oxidation on unmilled Pt(II)/rutile suspension (♦), compared with oxidation on the corresponding suspension milled for 5 min (■), or 60 min (▲).

pensions and caused only a small ($\sim 10\%$) decrease in the rate of reaction when the milling time was increased to 60 min. The differences between P25 and rutile are much smaller than previously reported for unmilled material [10] because milling increases the rate for rutile much more than it does for P25. The greater sensitivity to milling of NR is a function of the initially higher degree of aggregation, which is shown in the micrographs.

The effect of milling on the photocatalytic activities of nanoparticulate rutile and P25 broadly parallels the effect of milling on their optical properties. Milling of the nanoparticulate rutile significantly improved dispersion and activity for DCA degradation. Milling of P25 caused little change in dispersion or in photocatalytic activity. Since the probable mechanism of DCA oxidation at pH 3 involves direct hole transfer to the adsorbed dichloroacetate the possibility that milling increased DCA adsorption on nanoparticulate rutile was explored by comparing DCA adsorption before and after 60 min milling. In both cases $5.5 \pm 0.2\%$ of the initial DCA was adsorbed onto the rutile surface in 1 h. Therefore, the possibility that the increased catalytic activity was due to increased adsorption was excluded.

3.3. The effect of milling on the photocatalytic oxidation of DCA by Pt/TiO₂

The relative insensitivity of the transmission spectra to milling demonstrated that the milling did not significantly change the dispersion of P25 in aqueous DCA suspensions. The insensitivity of the photocatalytic oxidation of DCA by P25 to milling confirmed that milling with $\sim 200 \mu\text{m}$ ballotini did not introduce defects (of the type found after much heavier milling [17]), which can significantly reduce the activity of TiO₂. This made Pt/P25 a good candidate material for this study. However, because earlier studies had shown that the rate of DCA oxidation on rutile was greatly increased (approximately 35-fold) by the presence of Pt, milling experiments were also conducted on the Pt/NR catalysts.

The photoactivity of unmilled Pt/P25 and Pt/NR catalysts has been reported previously [7] and it was demonstrated that deposition of 0.38 wt% Pt(II) or Pt(0) on nanoparticulate rutile increased the rate of DCA oxidation on unmilled catalysts by factors of 37 and 33 respectively. The results shown in Fig. 5 demonstrate that

Table 1
The dependence on milling time of the rate constants for DCA oxidation by five different photocatalysts.

Sample	Rate constant ($\text{mol dm}^{-3} \text{ min}^{-1}$)			
	0 min milling	5 min milling	15 min milling	60 min milling
Rutile	1.04×10^{-5}	1.38×10^{-5}	1.59×10^{-5}	3.39×10^{-5}
0.38 wt% Pt(II)/rutile	3.77×10^{-4}	1.35×10^{-4}	–	1.15×10^{-4}
0.38 wt% Pt(0)/rutile	3.32×10^{-4}	–	–	1.50×10^{-4}
P25	1.59×10^{-4}	–	1.60×10^{-4}	1.43×10^{-4}
0.15 wt% Pt(II)/P25	2.66×10^{-4}	–	–	1.63×10^{-4}

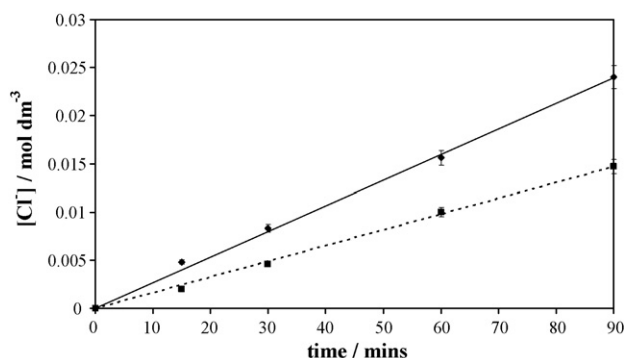


Fig. 6. DCA oxidation on unmilled Pt(II)/P25 suspension (◆), compared with oxidation on the corresponding suspension milled for 60 min (■).

milling Pt(II)/NR for 5 min decreases the photoactivity by ~60%, and that milling, for 1 h, results in an additional small decrease. A similar behaviour was observed for Pt(0)/NR, as summarized in Table 1. Thus milling Pt/NR caused a 2–3-fold decrease in activity, whereas milling the unplatinized NR increased activity by a factor of 3.2.

Platinum had a similar but lower effect on the photoactivity of Degussa P25; it increased activity by only 70% even though the amounts of platinum per square metre of TiO₂ surface were similar for the two catalysts. However, as shown in Fig. 6, milling the Pt(II)/P25 photocatalyst for 1 h reduced the photoactivity. As shown in Table 1, milling the Pt/P25 catalyst eliminated any benefit associated with presence of Pt; the milled Pt/P25 catalyst has the same activity as the unplatinized P25 material. Thus, milling reduced the activity of all three Pt treated catalysts, a pattern that is quite different to that observed for the non-platinized materials.

4. Discussion

4.1. The effect of dispersion on the measured photocatalytic activity for DCA oxidation by unplatinized nanoparticulate rutile and P25

The key conclusion from these results for DCA oxidation is that there is no evidence of significantly decreased activity as the degree of dispersion of the TiO₂ photocatalyst increases. For P25, milling causes only very small changes in the UV–vis transmission spectra and these are mirrored by very small (<10%) decreases in photocatalytic activity. For nanoparticulate rutile (NR), milling causes an increase in activity. The different pattern of results for P25 and NR is attributed to NR's higher initial degree of aggregation/flocculation which is broken down on milling.

By contrast, milling has been shown to decrease the measured rate of the photocatalytic oxidation of propan-2-ol by both P25 and nanoparticulate rutile [16,19]. Changes in TiO₂ dispersion have different consequences for propan-2-ol and for DCA because the two reactions have a different dependence on UV intensity, I . Propan-2-ol oxidation varies as $I^{0.5}$, the square root of the UV intensity [1] and consequently the measured oxidation rate decreases as the TiO₂ dispersion improves, as discussed earlier [16,19]. DCA oxidation at pH 3 varies as I^1 and when the measured dispersion improves there is an increase in the measured reaction rate. The detailed reasons for this increase have not been delineated but it may occur because initially the available surface is not well utilized in the initial, poorly dispersed nanoparticles.

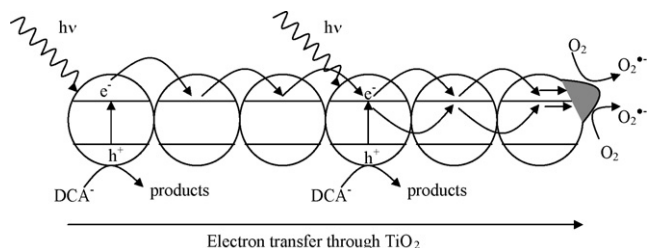
Although a 1:1 correspondence between the dispersion of TiO₂ in propan-2-ol and the dilute aqueous DCA cannot be expected, the results of both studies imply that nanoparticulate rutile is more heavily aggregated than the P25. However, both suspensions were white and significantly scatter visible radiation. Since the surface

area measurements imply single crystal sizes (of 12 nm for NR or 30 nm for P25) which would be too small to scatter visible radiation there must be significant residual aggregation or flocculation even in the P25.

4.2. The effect of dispersion on the measured photocatalytic activity for DCA oxidation by platinized nanoparticulate rutile and P25

The BET surface area of P25 implies 30 nm diameter primary particles, assuming that they are spherical. It follows that there are 1.8×10^{16} primary particles in 1 g of catalyst. The electron micrographs suggest that the Pt crystallites are quite large, of the order of 12 nm, and an assumption that these form hemispherical islands on the P25 leads to an estimate of 1.55×10^{14} platinum islands (based on the 0.15 wt% Pt sample). This number is about two orders of magnitude less than the number of P25 particles. For the 0.38% Pt/NR the corresponding figure is one platinum island per 30 TiO₂ particles. Even though the estimate is very approximate it is difficult to avoid the conclusion that there are more P25 particles than there are Pt islands. Despite this, Pt increased the DCA photo-oxidation rate by a factor of 1.6, on P25, or ~35, for nanoparticulate rutile. (The relative size of these effects has been discussed elsewhere [7].) One hypothesis to explain this unexpected result is that our electron micrographs are of insufficient quality to detect small platinum particles, and that there are enough undetected small particles for each primary particle of TiO₂ to have at least one platinum particle in intimate contact. A second hypothesis is that, although few, 1 in 100, primary particles of P25 have a platinum island, the enhancement caused by platinum is so large that there is still a net enhancement. (For platinum on 3% of the rutile primary particles an enhancement by 1000 would be required to give the observed factor of ~35.) Although neither hypothesis can be excluded absolutely, the marked decrease in photocatalytic activity when dispersions of platinized titania are milled suggests that neither is significant. The activity of 0.15 wt% Pt(II)/P25 milled for 60 min was only 48% of that of the unmilled Pt(II)/P25 and almost identical to the activity of the unplatinized P25. The activity of milled 0.38 wt% Pt(II)/rutile was 30% of the unmilled catalyst, and that of 0.38 wt% Pt(0)/rutile was 45% of the unmilled catalyst. (By contrast, the activity for milled unplatinized P25 was 90% of the unmilled sample, and that of milled NR was larger ($\times 3.25$) than that of the unmilled NR.) Taken together, the results imply that the effects due to platinum are greatest when the clustering (flocculation or aggregation) of the particles is greatest. However, it is unclear that either of the above hypotheses would be influenced greatly by such changes.

Instead, it is suggested that the observed results are an example of the *antenna effect* described by Wang et al. [15] who postulated that “energetic coupling throughout a long chain of titania nanoparticles will enable energy and/or charge-carrier transfer from the particle where the initial photon absorption takes place to the particle where the electron transfer process finally occurs”. The idea is schematically illustrated by Scheme 1 which represents the flocculate as a chain or antenna. Although the true structure is more complex – a three dimensional fractal assembly – the antenna model reflects the tendency of TiO₂ to form linear chains – as illustrated by the electron micrograph of an air flocculate shown in Fig. 7. This tendency to form flocculates in which the particles are aligned along the c -axis of the TiO₂ crystals is often considered to be a consequence of the greater polarizability of the crystal along this axis. This greater polarizability is reflected by the anisotropic dielectric constant of rutile (170 parallel to the c -axis; 86 perpendicular to the c -axis [20]). However, the key concept here is the possibility that electron transfer from crystal to crystal is induced by the platinum particles which are located on the minority of



Scheme 1. Representation of 'antenna' effect by which absorption of a photon at the primary particle at one end of a flocculate or agglomerate generates a conduction band electron which is transferred between particles to a distant platinum island located on another particle.

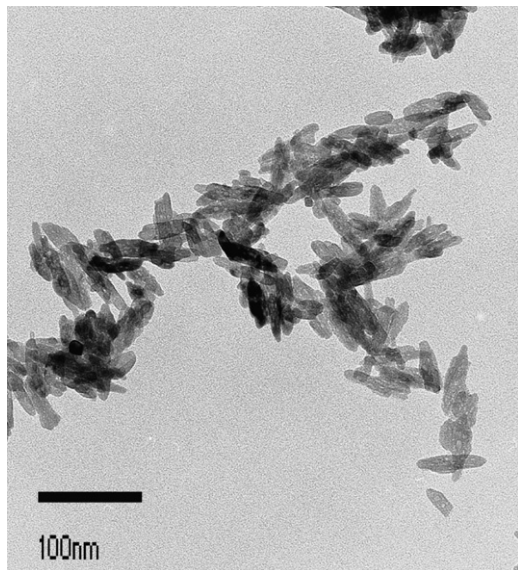


Fig. 7. Transmission electron micrograph obtained by dusting the high area rutile onto the microscope grid. The image shows the tendency of the rutile to form linear flocculates.

TiO₂ crystals. This basic concept is not significantly influenced by changes in the flocculate morphology.

On milling the flocculates or weak aggregates would be partially broken down – as is implied by the change in the optical density of the suspension on milling. This break-down reduces the possibility of electron transfer, and therefore reduces the ability of the unevenly distributed platinum to increase photocatalytic activity by trapping electrons. The results in Table 1 show that after 60 min milling the activities of the more heavily aggregated Pt/NR catalysts are still three to four times that of the unplatinated rutile but that the activity of platinized Pt/P25 falls to the level of the unplatinated P25.

The argument suggests that electrons in the conduction band of one TiO₂ particle can transfer to the conduction band of a neighbouring particle – a process that would not be routinely predicted. The hypothesis should therefore be tested further, perhaps by comparing the effects of milling on samples with varying levels of platinum, since the size of the effect is likely to vary with the ratio

of the number of primary TiO₂ particles to the number of platinum islands.

5. Conclusions

Thus work emphasizes the importance of particle dispersion in controlling the activity of photocatalytic suspensions. It was previously reported that the activity for propan-2-ol oxidation by unplatinated titania varied as the square root of UV intensity and this dependence was argued to be the cause of the reduction in the rate of acetone formation as the particle dispersion improved. By contrast, DCA oxidation at pH 3 has been demonstrated to vary linearly with light intensity and there is no indication that improved dispersion of unplatinated titania reduces the photocatalytic activity. The comparison demonstrates that the effect of particle dispersion depends on the mechanism of the oxidation reaction.

The study of DCA oxidation by platinized titania does however show a decrease in activity with improved dispersion. This decrease would arise if the activity increase associated with platinization required electron transfer along a titania antenna to the relatively few TiO₂ particles on which Pt islands have formed. Breaking the titania–titania contacts would reduce the possibility of electron transfer and would therefore decrease the activity.

Acknowledgements

We thank EPSRC and ICI Uniqema (now Croda Chemicals) for support of this work through the provision of a CASE studentship and thank Drs. Lorna Kessel and Ian Tooley of Uniqema/Croda for the provision of the high area rutile and for many helpful discussions.

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